

PCT

PTO/PCT Rec'd 29 JAN 2001
WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau



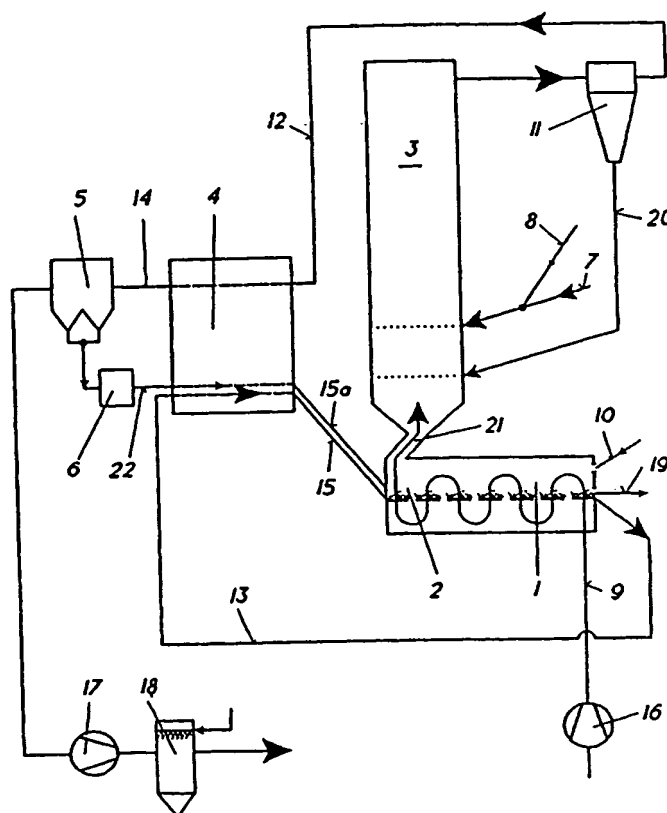
INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁷ : C10J 3/84, 3/54, 3/56		A1	(11) International Publication Number: WO 00/06672
			(43) International Publication Date: 10 February 2000 (10.02.00)
(21) International Application Number: PCT/CH99/00313 (22) International Filing Date: 9 July 1999 (09.07.99) (30) Priority Data: 98810727.2 29 July 1998 (29.07.98) EP (71) Applicant (for all designated States except US): "PATEL-HOLD" PATENTVERWERTUNGS- & ELEKTRO-HOLDING AG [CH/CH]; Kurt Brunner, Bankstrasse 21, CH-8750 Glarus (CH). (72) Inventors; and (75) Inventors/Applicants (for US only): TOQAN, Majed [US/DE]; Landgraf Gustav Ring 24, D-61348 Bad Homburg (DE). SRINIVASACHAR, Srivats [US/US]; 10 Podunk Road, Sturbridge, MA 01566 (US). KIETLINSKI, Krzysztof [PL/PL]; Ratuszowa 7/1, PL-82-300 Elblag (PL). (74) Agent: KLEIN, Ernest; Sandstrasse 24, CH-5416 Kirchdorf (CH).		(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published With international search report.	

(54) Title: METHOD OF PRODUCING A CLEAN GAS FROM A HYDROCARBON

(57) Abstract

In a method of producing a clean gas from hydrocarbons, hot air and steam are mixed in a reaction zone with carbonaceous residue, whereby carbon reacts with oxygen to form CO₂ and CO under heat release. Hydrocarbon is added to release moisture and volatile and to have reacted volatile and carbon to CO and H₂, the sulfur of the hydrocarbon being mainly converted into H₂S. A sulfur sorbent is added and is converted into CaO, which CaO reacts with H₂S and COS to solid CaS. At the exit of the reaction carbonaceous residue is separated from the fluid and returned to the reaction zone. The gas is fed into a gas cooler, in which it is cooled by cold solids. The solids consist on one hand of ash being cooled with the air prior to the air entering into the reaction zone and on the other hand of ash and carbonaceous residue filtered out of the reduced gas downstream the gas cooler. The latter solids are size-enlarged prior to their entering the gas cooler.



Method of producing a clean gas from a hydrocarbon

Field of the invention

The invention relates to a method of producing a clean gas in a reaction zone by mixing hot air and steam with carbonaceous residue, adding hydrocarbon to release moisture and volatile and to have reacted volatile and carbon to CO and H₂.

Discussion of Background

The production of fuel gas from hydrocarbon like coal is operated at the present time by injecting cold reactants and/or steam into a gasifier and transferring a major portion of the sensible heat in the gasification products to a water/steam mixture. This is necessary to enable reliable operation of downstream gas cleaning equipment. Consequently the conversion of coal to the product gas in terms of the energy content is not maximized.

Summary of the invention

Accordingly, one object of the invention is to provide a novel method and plant which maximizes the production of clean "reduced" gas from the feed hydrocarbon with minimal transfer of heat out of the involved system.

This is achieved, according to the invention, by means of the features of patent claims 1 and 10.

The advantages of the invention are to be seen, inter alia, in a considerable reduction of the plant and operating costs, due to a very high calorific value conversion and in the elimination of indirect contact heat exchangers.

Brief description of the invention

A more complete appreciation of the invention and many of the attendant advantages thereof will be readily obtained as the same becomes better understood by reference to the following detailed description when considered in connection with the accompanying drawing, which illustrates diagrammatically an exemplary embodiment of the invention with coal as hydrocarbon. Only the elements essential for understanding the invention are shown. Arrows illustrate the flow direction of the working media.

Description of the preferred embodiment

Referring now to the drawing, the equipment necessary for performing the gas production consists mainly of three blocks, namely a gasifying device 3, a gas/solid heat exchanger 4 and an combined ash cooler/oxidizer 1, 2.

Via a fan 16 ambient air is introduced in the ash cooler 1. In order to increase the amount of oxygen atoms and in the same time reduce the amount of air, water is also introduced into the cooler at its cold end via water supply 10. This water is evaporated in the air stream during its travel through the cooling device. This device may be a gas/solid heat exchanger of the grid type or of the fluid bed type. The air is heated up to about 500-900°C. The lower value is chosen, if it is intended to have a catalytic reaction further downstream. The solids entering the cooler 1 at its hot side consist mainly of inert ash, carbon and of CaS and CaO.

They have an inlet temperature of about 600°C and leave the cooler with a temperature of about 100°C. The size of the solids is at least approximately 500 μm which avoids particles being entrained with the air leaving the cooler at its hot end. By entering the apparatus 1, in an oxidizing sector 2 the unburned carbon and CaS particles are first oxidized by the hot air/steam mixture into CO_2 and CaSO_4 . Other components of the hot material, i.e. unoxidized gases like CO, H_2S and COS as well as sulphided sorbents like CaS and FeS are also oxidized in this area. It might be that the unburned carbon and CaS particles are also oxidized by the hot air/steam mixture into CaO and SO_2 . In order to avoid that significant amount of SO_2 penetrates in the following reactor, it is appropriate to arrange the heat exchanger surfaces and to have the air/steam mixture circulated in the sector 2 so as to obtain as a last process in the oxidizer always mainly CaSO_4 .

From this oxidizing area 2, which is the hot side of the ash cooler 1, the air/steam mixture enters a reactor 3 via a hot air supply 21. Depending on the apparatus type, the mixture can be introduced into the reactor on different levels. In the example shown on the drawing, in which the reactor is an upright gasifier with a flow stream from bottom to top, the mixture is introduced at the bottom. The reactor is provided with two other inlets. One carbonaceous residue supply line 20 and one common inlet for coal 7 and sulfur sorbent 8.

In the present example the carbonaceous residue is char which is partially gasified coal. It enters the reactor 3 with a temperature of about 700°C. It reacts with the oxygen of the air/steam mixture to form CO_2/CO and releases heat.

Downstream of the char inlet, the coal to be gasified is introduced into the reactor 3. This coal can be either crushed or pulverized. Like the air, coal may be injected on different levels of the reactor. The same inlet is preferably used to introduce sulfur sorbent, which can be pulverized limestone or dolomite. Coal and sorbent may be transported by any suitable means, i.e. by steam; in a pre-

ferred embodiment, the produced reduced gas itself transports the solids. If the coal is in form of crushed material with a size of approximately 6 mm, it can be fed by gravity. The adding of coal in the reactor results in a moisture and volatile release. A reaction of volatile and carbon occurs with the steam, the CO_2 and remaining O_2 (if any) to form CO and H_2 .

Thus at the exit of the reactor 3 there is mainly CO and H_2 to be found together with N_2 from the air and trace amounts of CO_2 and H_2O in vapor form. Also present are char and ash. The temperature at the exit of the reactor is in the range of 400-700°C, again depending on the entry temperature of the air due to any possible catalytic treatment downstream.

If limestone is used as a sulfur sorbent in the reactor, CaCO_3 is converted into CaO . The sulfur in the coal is converted mainly into H_2S and in trace quantities into COS . Most of the H_2S and COS react with CaO to form solid CaS . Thus at the exit of the reactor, the calcium sorbent is present as CaS and CaO .

Downstream the reactor a particulate separation device 11 is provided. This separator could be a cyclone designed to separate the predominant char from the remaining components. Since the size of the ash is typically smaller than 30µm it will escape the cyclone, while the char, which is greater than 100µm, will be retained in the cyclone. This separated char is returned via the supply line 20 into the reactor, while the remaining components, especially the reduced gas is forwarded to a gas cooler 4.

The reduced gas is supposed to leave the gas cooler 4 with a temperature of about 200°C. Downstream the gas cooler a solids filter 5 is provided in the line 14 to remove from the gas fine ash and char, as well as CaS and CaO that has not been separated in the gas cooler 4. This filter is supposed to remove all the remaining solids from the gas.

A further fan 17 is installed in the gas line 14, preferably on the clean side of the filter 5. Its purpose is to control the pressure in the system close to atmospheric conditions.

Depending on the utilization of the gas, a further gas cooler 18 may be provided in the gas line 14 downstream the fan 17, if a wet electrostatic participator has not been used upstream as a filtering element. To cool the gas down to 30°C, it is recommended to use a water spray cooler.

The filter 5 could be a fabric filter, an electrostatic participator or a wet electrostatic participator. The use of the latter provides following advantages: beside the particulate removal a further cooling of the gas, the removal of ammonia, tar and hydrogen cyanide that might have been produced in the reactor 3.

The further treatment of the solids removed from the filter 5 is a major feature of the present invention.

The gas cooler 4 is a gas/solids heat exchanger and might be constituted of a series of cyclones. Therein solids and gas flow in a predominating counter-current manner. The minor part of cold solids fed into the gas cooler is taken from the exit of the filter 5 via feed line 22. As the size of the solids exiting the filter is smaller than 50µm, they have to be size-enlarged in order to enable retention within the cyclones. This agglomeration occurs in a pelletizer 6, in which pellets having a size of approximately 1-5 mm are produced. The solids are introduced in the gas cooler 4, in which they are heated up to about 600°C. At the exit of the gas cooler, they are fed into the ash cooler 1 via the heated solids line 15a.

In a preferred embodiment, the major part of cold solids to be fed into the gas cooler are solids exiting the ash cooler 1 being recycled unchanged into the gas

cooler 4 via 13. This means that only the solids exiting the filter 5 have to be pelletized. This is based on the fact, that the size of the solids being cooled down in the ash cooler 1 is great enough to be retained in the gas cooler 4 while flowing through the series of cyclones. As shown in the drawing, accordingly both solids from filter 5 and from ash cooler 1 are separately introduced in the gas cooler. Moreover they each cross the gas cooler in a separate path being each heated up therein to about 600°C. The separate paths are maintained as a heated solids line 15, 15a throughout the further flow of this solids.

Due to the permanent adding of coal and sulfur solvent during operation, an equivalent amount of solids has to be removed from the system. This occurs preferably in a disposal line 19 connected to the exit of the ash cooler 1.

As described below in an example, the amount of the solids exiting the filter 5 and flowing through line 15a corresponds approximately to the amount of material to be disposed. Accordingly it is preferable to also keep separated by a partition this solids from the main solids flow in line 15 within its travel through the ash cooler 1 and to dispose it via the line 19.

The invention may be illustrated in more detail with reference to a numerical example: it goes without saying that absolute values cannot be specified in connection with the said numerical values with regard to the dimensioning of the involved apparatus and in particular the reactor and the gas cooler, since absolute values are in any case not meaningful enough on account of their dependence on all too numerous parameters. The sole determining factor for the design is that minimal transfer of heat out of the involved system is realized.

The amount of injected coal via line 7 be 19.5 kg/sec, the coal having a lower heating value of about 25 MJ/Kg and containing about 2.5 kg H₂O. The amount of injected sulfur sorbent, i.e. limestone via line 8 be 3 kg/sec. Via a fan 16, about 45 kg/sec of air are sucked in the system. Water in the amount of 5 kg/sec

is added at the cold side of the ash cooler via water supply 10. All these components are introduced under ambient conditions.

The amount of circulated inert solids through the gas cooler 4 and the ash cooler 1 via path 13, 15 is about 75 kg/sec. The amount of solids captured at the exit of filter 5, pelletized and transported through the gas cooler and the ash cooler in an own path 15a and disposed via the line 19 is about 5.5 kg/sec. It is assumed that 0.5 kg/sec of this solids are burned out during oxidation in the ash cooler and flow as a gas into the reactor 3, thus remaining in the cycle.

As a result the reduced product gas downstream the fan 17 is at an amount of about 67.5 kg/sec, the gas having a heat value of 6.7 MJ/kg. A small amount of the product gas is kept in the system as a transportation means for the pulverized coal and sorbent.

Instead of introducing the whole amount of hydrocarbon into the reactor, in a first variant of the invention, a small amount of the hydrocarbon, i.e. coal might be injected in a burner located in the ash cooler. This feature allows a temperature control within the ash cooler.

In a second variant, the sorbent, i.e. limestone or dolomite might be injected into the ash cooler instead into the reactor 3. If this sorbent is pulverized, the size must be fine enough to be entrained by the air stream. Again CaCO_3 is converted into CaO ; a small portion of unreacted CaO forms CaSO_4 with SO_2 in the ash cooler. This feature allows calcining the sorbent and providing a longer residence time for CaO inside the downstream reactor 3, which improves the sulfur capture.

In a further variant, the air/steam mixture as well as the coal might be introduced into the reactor at several different locations, which allows a better temperature control inside the reactor and a still higher conversion efficiency.

Of course, the invention is not restricted to the plant shown and described. The invention can be used irrespective of the type and design of the reactor. This reactor could be as well an apparatus with entrained flow, if a pulverized fuel is used or with fluidized bed, if crushed fuel is used. Instead of cyclones, separating apparatus with moving bed could be used as well.

Obviously, numerous modifications and variations of the present invention are possible in light of the above teachings. It is therefore to be understood that, within the scope of the appended claims, the invention may be practiced otherwise than as specifically described herein.

LIST OF DESIGNATIONS

- | | |
|----|--|
| 1 | air heater (gas/solid heat exchanger) |
| 2 | Oxidizer |
| 3 | Gasifier |
| 4 | reduced gas cooler |
| 5 | solid filter |
| 6 | pelletizer |
| 7 | coal feed line |
| 8 | sulfur sorbent line |
| 9 | air supply |
| 10 | water supply |
| 11 | particulate separation device, cyclone |
| 12 | hot gas line |
| 13 | cold solids line |
| 14 | cold gas line |
| 15 | heated solids line |
| 16 | pushing fan |
| 17 | pulling fan |
| 18 | gas cooler |
| 19 | removal of ash |
| 20 | carbonaceous residue supply line |
| 21 | hot air supply to 3 |
| 22 | feed line from 5 to 4 |

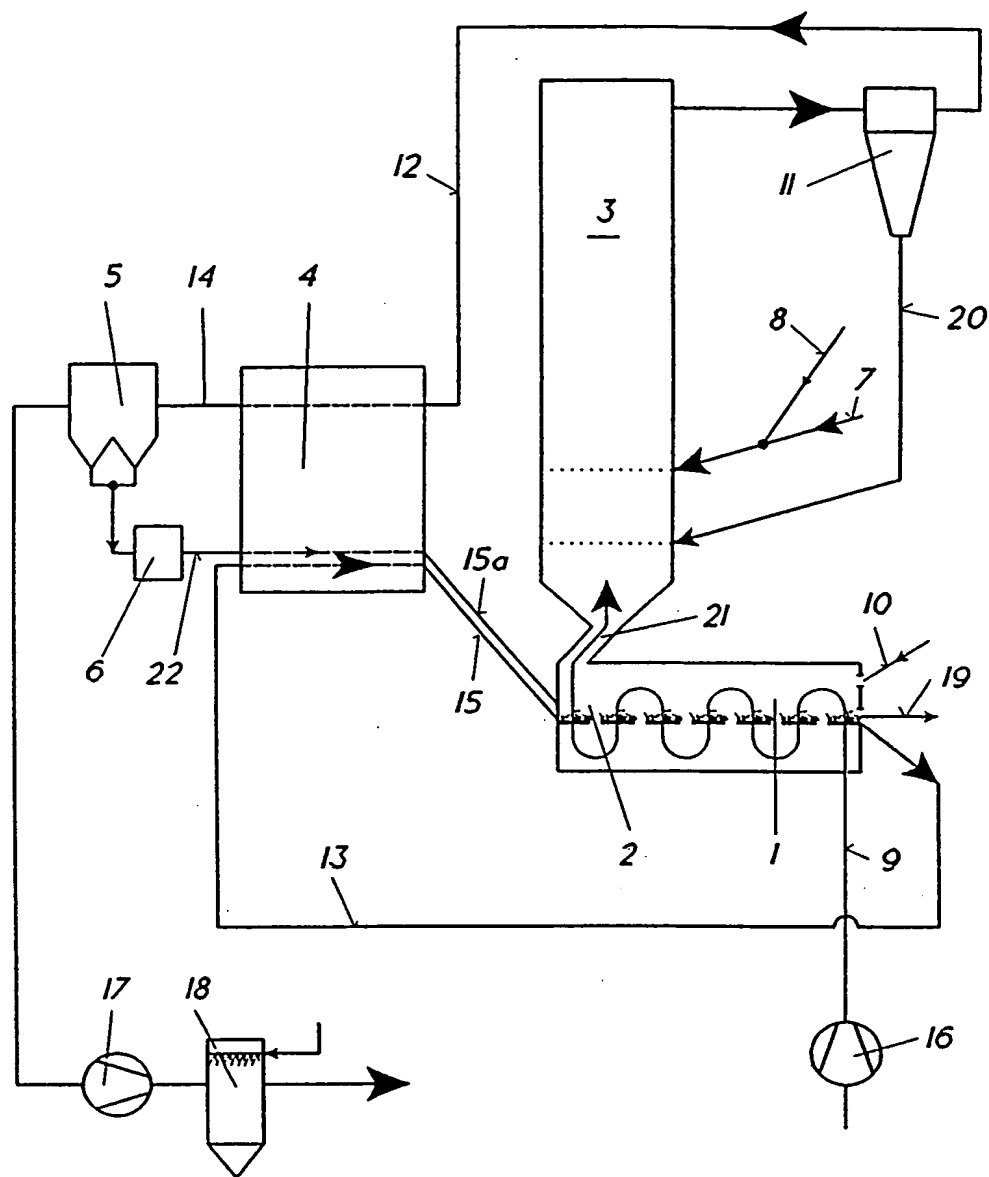
Claims

1. A method of producing a clean gas from hydrocarbons, comprising the steps of
 - in a reaction zone mixing hot air and steam with carbonaceous residue whereby carbon reacts with oxygen to form CO_2 and CO under heat release, adding hydrocarbon to release moisture and volatile and to have reacted volatile and carbon to CO and H_2 , the sulfur of the hydrocarbon being mainly converted into H_2S , adding a sulfur sorbent being converted into CaO, which CaO reacts with H_2S and COS to solid CaS,
 - at the exit of the reaction zone separating at least the predominant of the carbonaceous residue from the fluid and returning it to the reaction zone,
 - feeding the gas into a gas cooler, in which it is cooled preferably in countercurrent by cold solids, the solids consisting on one hand of ash being cooled with the air prior to the air entering into the reaction zone and on the other hand of ash and carbonaceous residue filtered out of the reduced gas downstream the gas cooler, the latter solids being size-enlarged prior to their entering the gas cooler .
2. A method according to claim 1, characterized in that the hydrocarbon and the sulfur sorbent are commonly injected into the reaction zone.
3. A method according to claim 2, characterized in that the hydrocarbon and the sulfur sorbent are pulverized and are transported by means of the produced reduced gas.

4. A method according to claim 1, characterized in that steam is produced by introducing water into a heat exchanging zone upstream the reaction zone, where the water evaporates in the air stream, the air stream being heated by the hot solids exiting the gas cooler and the air/steam mixture oxidizing unburned carbon, sulphided sorbent and unoxidized gases.
5. A method according to claim 4, characterized in that some of the hydrocarbon is injected into a burner of the heat-exchanging zone.
6. A method according to claim 4, characterized in that the sulfur sorbent is introduced into the heat-exchanging zone.
7. A method according to claim 1, characterized in that the air/steam mixture as well as the hydrocarbon is fed into the reaction zone in at least one location.
8. A method according to claim 1, characterized in that the air heating/solids cooling, the reaction with hydrocarbon and sulfur sorbent, the solids separation, the gas cooling/solids heating and the filtering is performed under at least approximately atmospheric pressure.
9. A method according to claim 1, characterized in that the ash filtered out of the reduced gas downstream the gas cooler is disposed after having being heated in the gas cooler and cooled in the heat exchanging zone upstream the reaction zone.

10. A plant for performing the method according to claim 1 comprising
 - a hydrocarbon feed line (7), a sulfur sorbent feed line (8), a hot air supply (21) and a carbonaceous residue supply line (20), all connected to a reactor (3), the exit of the reactor (3) being connected to a particulate separation device (11),
 - a gas cooler (4) being connected at it's inlet side via a hot gas line (12) to the exit of the particulate separation device (11) and via a cold solids line (13, 22) to a solids supply, and being connected at it's outlet side via a cold gas line (14) to a solids filter (5) and via a heated solids line (15, 15a) to a gas/solids heat exchanger (1),
 - the solids outlets of the filter (5) and of the gas/solids heat exchanger (1) forming the solids supply to the gas cooler (4).
11. A plant according to claim 10, characterized in that the gas/solids heat exchanger (1) comprises an oxidizer (2) at its hot end.
12. A plant according to claim 10, characterized in that the gas/solids heat exchanger (1) comprises from it's inlet to it's outlet two solids flow paths separated by a partition and being fed each with solids from a separate heated solids line (15, 15a).
13. A plant according to claim 10, characterized in that the gas cooler (4) comprises a series of cyclones.
14. A plant according to claim 10, characterized in that a solids size-enlarging apparatus (7) is provided in the feed line (22) between the solids outlet of the filter (5) and the inlet of the gas cooler (4).

15. A plant according to claim 10, characterized in that pressure control in the system is performed by a fan (17) installed in the cold gas line (14) downstream the filter (5).
16. A plant according to claim 10, characterized in that the filter (5) is a wet electrostatic particulator.



INTERNATIONAL SEARCH REPORT

International Application No

PC/CH 99/00313

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C10J3/84 C10J3/54 C10J3/56

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C10J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	GB 1 528 623 A (STORA KOPPABERGS BERGSLAGS) 18 October 1978 (1978-10-18) the whole document	1,2,7,8, 10
A	US 4 198 212 A (TSAO) 15 April 1980 (1980-04-15) the whole document	1,9
A	PATENT ABSTRACTS OF JAPAN vol. 006, no. 015 (C-089), 28 January 1982 (1982-01-28) & JP 56 139587 A (AGENCY OF IND SCIENCE & TECHNOL), 31 October 1981 (1981-10-31) abstract	1,4,9-11
A	EP 0 725 127 A (METALLGESELLSCHAFT) 7 August 1996 (1996-08-07) page 3, line 27-46	1

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- "&" document member of the same patent family

Date of the actual completion of the international search

29 September 1999

Date of mailing of the international search report

06/10/1999

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Meertens, J

INTERNATIONAL SEARCH REPORT

International Application No.

PCT/CH 99/00313

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 384 454 A (AHLSTRÖM CORP.) 29 August 1990 (1990-08-29) page 5, column 7, line 30 -page 6, column 9, line 10 ----	1, 10, 14
A	EP 0 227 197 A (SHELL) 1 July 1987 (1987-07-01) -----	

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PL/CH 99/00313

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
GB 1528623 A	18-10-1978	SE 390420 B AU 497855 B AU 8533675 A CA 1093821 A DE 2543500 A FR 2286874 A SE 7412370 A	20-12-1976 18-01-1979 07-04-1977 20-01-1981 15-04-1976 30-04-1976 02-04-1976
US 4198212 A	15-04-1980	NONE	
JP 56139587 A	31-10-1981	JP 1187032 C JP 58017795 B	20-01-1984 09-04-1983
EP 725127 A	07-08-1996	DE 19503438 A AT 173005 T DE 59600749 D	08-08-1996 15-11-1998 10-12-1998
EP 384454 A	29-08-1990	FI 890833 A AT 80908 T JP 1963951 C JP 2290406 A JP 6097082 B US 4969930 A	23-08-1990 15-10-1992 25-08-1995 30-11-1990 30-11-1994 13-11-1990
EP 227197 A	01-07-1987	NONE	